Pergamon

*Tetrahedron*, Vol. 52, No. 7, pp. 2481-2488, 1996

0040-4020/96 $15.00 + 0.00

0040-4020(95)01069-6

# Photolytic Double Decarbonylation Route to Highly Substituted Indenes and Benzene Derivatives

**Abraham Thomas, Gopinathan Anilkumar and Vijay Nair***

Organic Chemistry Division
Regional Research Laboratory (CSIR)
Trivandrum 695 019, INDIA

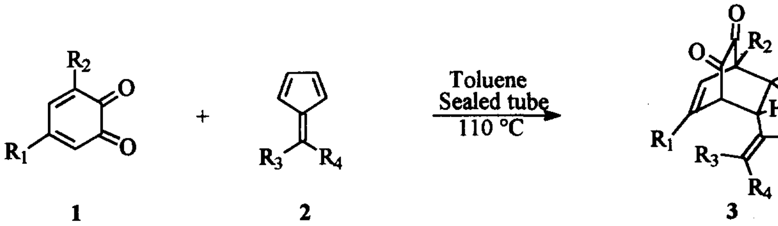
*Key words:* Bicyclic 1,2-diones; photolytic double decarbonylation; DDQ assisted dehydrogenation; Benzofulvenes.

*Abstract:* UV irradiation of cyclohexane solution of a 4,7-ethanoindene-8,9-dione derivative led to a facile extrusion of two molecules of carbon monoxide to give a dihydroindene along with its dehydrogenated product, a methylene indene (benzofulvene). The inseparable mixture of dihydroindene and benzofulvene on treatment with DDQ underwent dehydrogenation and equilibration to afford the latter as a single stereoisomer in high yield. The double CO extrusion process is a general reaction and it has been applied to the synthesis of a number of benzofulvenes and highly substituted benzene derivatives.

Indene derivatives, especially benzofulvenes, have received attention due to their interesting properties in electrochemical reduction reactions.[1] The current method for the synthesis of benzofulvenes utilizes a cationic cyclization of aryl substituted but-1-ene-3-ynes.[2] This reaction is of limited scope and it suffers from a number of drawbacks, which include the use of expensive and/or difficultly accessible reagents as starting materials and also the success of the cyclisation step largely relies on the geometry and the substitution pattern of the alkene. As a part of the investigations on the cycloaddition of *o*-quinones, we have recently reported the synthesis of a series of 4,7-ethanoindene-8,9-dione derivatives **3**[3,4] and the latter appeared to be ideal substrates for exploring photochemical decarbonylation reaction[5]; conceivably double extrusion of CO from these compounds would lead to the benzofulvenes **5** *via* the dihydroindene **4**[6]. An isolated example of photodecarbonylation of adducts derived from *o*-quinones and symmetrical diaryl fulvenes to benzofulvenes has been reported.[4a] We have investigated the scope of the photodecarbonylation reactions of sterically hindered bridged diones of the general structure **3** and **7** in detail and our results are described here.

The starting materials **3a-h** (Scheme 1) required for the present investigation were prepared according to our reported[3] procedure involving the cycloaddition of *o*-quinones with substituted fulvenes. The addition of *o*-quinones to unsymmetrical fulvenes afforded small amounts of *exo* isomer along with the major *endo* isomer; these were separable by careful fractional crystallization. $^1$H nmr and GCMS analyses suggested that both *exo* and *endo* isomers existed as a mixture of geometrical isomers (*E* & *Z*) in the case of **3d-h**.

Initially we investigated the decarbonylation of the bicyclic adduct **3a**. The α-diketone **3a** in degassed cyclohexane solution on absorption of UV light [$\lambda_{max}$ 284 nm ε, 17,960] from a medium pressure mercury lamp (pyrex filter) for 1h underwent clean and efficient photolytic decarbonylation (scheme 2)[7]. Analysis of the crude reaction mixture by GCMS showed the presence of two compounds differing in 2 mass units ($M^+$ 392 and 394 with retention times 22.05 and 21.51 min. respectively). They were discerned to be the diene **4a** and the benzofulvene **5a** from spectral data. As expected the IR spectrum of the mixture was devoid of any carbonyl absorption.



**3a** $R_1 = R_2 =$ t-Bu, $R_3 = R_4 =$ Ph

**3b** $R_1 =$ t-Bu, $R_2 =$ H, $R_3 = R_4 =$ Ph

**3c** $R_1 =$ H, $R_2 = OCH_3$, $R_3 = R_4 =$ Ph

**3d** $R_1 = R_2 =$ t-Bu, $R_3 =$ H, $R_4 =$ Ph

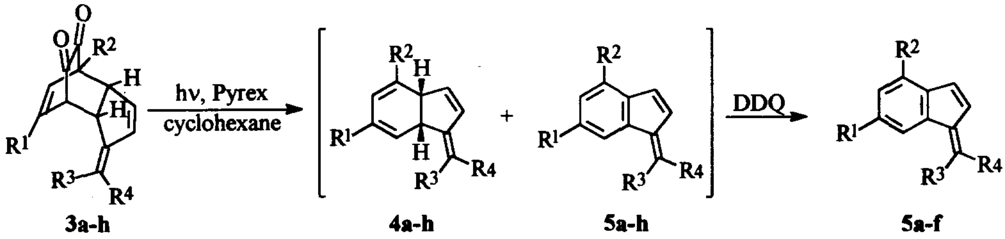
**3e** $R_1 =$ t-Bu, $R_2 =$ H, $R_3 =$ H, $R_4 =$ Ph

**3f** $R_1 = R_2 =$ t-Bu, $R_3 =$ H, $R_4 = 4\text{-}MeOC_6H$

**3g** $R_1 = R_2 =$ t-Bu, $R_3 = CH_3$, $R_4 =$ Ph

**3h** $R_1 =$ t-Bu, $R_2 =$ H, $R_3 = CH_3$, $R_4 =$ Ph

**Scheme 1**



**Scheme 2**

The $^1H$ nmr spectrum of the mixture was in agreement with the assigned structre; the two *cis* protons on the $sp^3$ carbon atoms of **4a** appeared as a multiplet at δ 2.85 - 3.20. The *cis* stereochemistry of **4a** is correlated to that of the starting adduct **3a**. Attempts to separate the products by column chromatography resulted in very poor resolution owing to the highly nonpolar nature of the products; chromatography using a $AgNO_3$-silica gel column failed as well. After much fruitless effort to separate the mixure, we considered a dehydrogenation reaction which would transform all the dienes present in the mixture to benzofulvene **5a**. Treatment of a mixture of **4a** along with its coproduct **5a** with DDQ in refluxing benzene afforded the fully aromatic compound **5a** in good yield. The $^1H$ nmr spectrum of **5a** was free of the signal at δ 2.85-3.20 which clearly suggested that oxidation of diene to benzofulvene **5a** has occurred. The reaction was found to be applicable to other α-diones and the results obtained along with reaction conditions are given in table1.

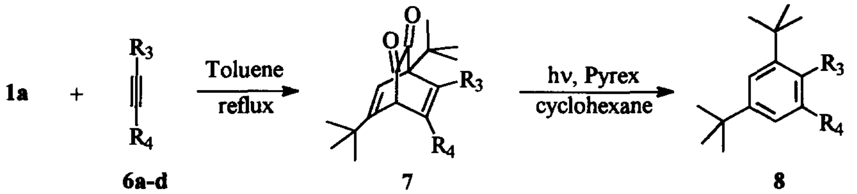
As mentioned earlier, **3d-h** exist as a mixture of *exo* and *endo* adducts. Irradiation of **3d** as a mixture under the conditions described earlier resulted in the rapid consumption of starting material and the reaction was complete in 1.5 h. GCMS analysis showed the presence of 4 products. Two of them had the $M^+$ ion at 316 and the other two had $M^+$ ion at 318, these were discerned to be the diene **4d** (92%) and the benzofulvene **5d** (8%) respectively. The mixture was directly subjected to dehydrogenation with DDQ in benzene. The product, isolated in excellent yield, on GCMS analysis showed only a single compound with $M^+$ ion at 316. Thus, the double signals observed for diene and benzofulvene in the GC were due to *E* and *Z* isomers. DDQ assisted dehydrogenation of the product not only led to its clean conversion to the benzofulvene but also to the isomerisation of the latter to a single stereoisomer[9].

**Table 1**: Photodecarbonylation and Dehydrogenation of Indenedione Derivatives

| Entry | Dione(**3**) | Reaction time(min) | Yield$^a$ (%) | Ratio(**4**:**5**)$^b$ | | DDQ oxidation | Yield(%) (**5**) |
|---|---|---|---|---|---|---|---|
| | | | | Diene(**4**) | Benzofulvene(**5**) | | |
| 1 | 3a | 60 | 92 | 89 | 11 | $C_6H_6$,reflux 5h | 80 |
| 2 | 3b | 90 | 85 | 2 | 98 | $C_6H_6$,reflux 5h | 76 |
| 3 | 3c | 50 | 40 | 49 | 51 | $C_6H_6$,reflux3.5h | 52 |
| 4 | 3d | 45 | 90 | 92 | 8 | $C_6H_6$,reflux 5h | 84 |
| 5 | 3e | 60 | 79 | 68 | 32 | $C_6H_6$,reflux 4h | 75$^c$ |
| 6 | 3f | 60 | 53 | 93 | 7 | $C_6H_6$,reflux 3h | 49 |
| 7 | 3g | 60 | 98 | 98 | 2 | see ref. 8 | - |
| 8 | 3h | 120 | 67 | 20 | 80 | $C_6H_6$, rt 0.5h | 58$^c$ |

a: combined isolated yield of **4** & **5**; b: GC analysis; c: mixture of *E*/*Z* isomers

The *E*-configuration of the exocyclic carbon-carbon double bond is determined by comparing the chemical shifts of the vinylic protons. Minimum energy calculations (MMX method) suggested that the *E*-isomer is preferred over the *Z* which is consistent with the stereochemical assignment. Compound **5f** was also isolated as a single stereoisomer. In the case of **5e** an equilibrium mixture (*E*:*Z* = 84:16) of benzofulvenes was isolated. This ratio did not vary even on prolonged heating in refluxing toluene. **3g** underwent photodecarbonylation quantitatively and afforded **4g** as a mixture of *E* and *Z* isomers (43:57) along with a trace amount of the benzofulvene **5g**. This mixture on treatment with DDQ did not give the expected product **5g**, instead a mixture of dienes in the ratio 60:40 was obtained. The reason why the DDQ reaction failed in this case is unclear. **3h** on irradition gave an *E* and *Z* mixture of diene **4h** and benzofulvene **5h** in the ratio 20:80. DDQ oxidation of this mixture gave the fulvene **5h** as a mixture of *E* and *Z* isomers in the ratio 21:79. As an extension of these studies we have carried out bisdecarbonylation of bicyclic adducts **7a-d** derived from 3,5-di-*tert*-butyl-*o*-benzoquinone and acetylenic compounds with a view to synthesise highly substituted benzene derivatives (scheme 3). The known adduct **7a** was prepared according to the literature procedure[10]. Addition of quinone **1a** to propargyl alcohol under identical conditions resulted in the formation of bicyclic adduct **7b** as a single regioisomer in 92% yield. The regiochemistry of **7b** is assigned on the basis of $^1H$ nmr spectrum.



**6,7,8a** $R_3 = R_4 = CO_2Me$
**b** $R_3 = H, R_4 = CH_2OH$
**c** $R_3 = Ph, R_4 = H$
**d** $R_3 = H, R_4 = Ph$

**Scheme 3**

Reaction of phenyl acetylene with **1a** gave regioisomeric mixture of adducts **7c** and **7d**. They were separated by fractional crystallization and both were subjected to photodecarbonylation reaction. Details of their preparation, spectral and analytical data are given in the experimental section.

As expected, irradiation of **7a** using a pyrex filter resulted in the clean conversion to the phthalic acid derivative **8a** in 82% yield. The bicyclic alcohol **7b** also underwent smooth decarbonylation to the symmetrical benzyl alcohol **8b** in excellent yield. The coupling constants of the aryl protons ($J$ = 1.6 Hz) confirm the regiochemical assignment. The products **8c** and **8d** were isolated in nearly quantitative yield. Evidently this method can be utilised for the synthesis of benzene derivatives that are not readily accessible by convensional methods. While the mechanistic details of the double photodecarbonylation remain unclear, it may be pointed out that in preliminary experiments with **7c**, no transient species were detected in laser flash photolysis[11].

In conclusion, we have developed an expeditious and general methodology for the synthesis of highly substituted benzofulvenes and benzene derivatives. The success of the approach rests on the easy availability of a series of α-diones and the tolerance of the decarbonylation reaction to various substitution pattern. It is anticipated that this method which is simpler, more general, and cost effective than the cationic cyclization procedure that is in vogue for the synthesis of benzofulvenes[2], will find wider applications.

**Acknowledgements:** AT and GA thank the CSIR, New Delhi for financial support. Thanks are due to Professor G. Mehta, University of Hyderabad for NMR spectra, Dr. T. Ravindranathan, National Chemical Laboratory, Pune for analytical data and Dr. Guenter K. Eigendorf, University of British Columbia, Canada for mass spectra. We thank Professor M. V. George and Dr. S. Das, Photochemistry Research Unit, RRL Trivandrum for their interest in this work.

## Experimental

Melting points were recorded on a Toshniwal capillary melting point apparatus and are uncorrected. IR spectra were run on a Perkin-Elmer Model 882 infrared spectrophotometer. Electronic spectra were recorded on a Shimadzu UV -2100 spectrophotometer. Unless otherwise mentioned, $^1H$ (90 MHz) and $^{13}C$ (22.4 MHz) nmr spectra were recorded on a JEOL EX-90 nmr spectrometer using tetramethylsilane as internal standard. High resolution $^1H$ nmr spectra were recorded on a Bruker-200 spectrometer. Mass spectra were run on a Finnigan MAT 8430 or Hewlett Packard 5890 mass spectrophotometer. All steady-state irradiations were carried out in an immersion well equipment using a Hanovia 450 W medium pressure mercury vapour lamp.

**Typical procedure for decarbonylation reaction: Synthesis of 1-(Diphenyl)methylene-4,6-bis(1,1-dimethylethyl)-3a,7a-dihydro-1*H*-indene 4a and 1-(Diphenyl)methylene-4,6-bis(1,1-dimethylethyl)-1*H*-indene 5a:** The adduct **3a** (300 mg, 0.66 mmol) was dissolved in cyclohexane (250 ml) and the solution was purged with argon for 10 minutes with stirring. It was then irradiated for 1.0 h using a 450 W mercury vapour lamp and a Pyrex filter. The solvent was evaporated under reduced pressure and the residue was directly charged onto a short length silica gel column. Elution with petroleum ether afforded a mixture of **4a** and **5a** (242 mg, 92%) as a viscous yellow liquid: $^{1}$H nmr (mixture of **4a** & **5a**) δ 7.05 - 7.70 (m), 6.42 - 6.70 (m), 2.85 -3.20 (m), 1.50 (s), 1.40 (s), 1.05 (s), 1.01 (s).

**Typical procedure for DDQ assisted dehydrogenation: Synthesis of 1-(Diphenyl)methylene-4,6-bis(1,1-dimethylethyl)-1*H*-indene 5a:** To a stirred solution of the mixture of diene **4a** and benzofulvene **5a** (200 mg) in dry benzene was added DDQ (230 mg, 1.01 mmol) and the mixture was gently refluxed with stirring for 5 h. Most of the solvent was evaporated under reduced pressure and the reaction mixture was directly charged onto a silica gel column. Elution with petroleum ether afforded 160 mg (80%) of the the benzofulvene **5a** as a golden yellow crystalline solid: mp 165 - 166 °C; IR (KBr) 2982, 2884, 1602,1492 cm$^{-1}$; $^{1}$H nmr (200 MHz) δ 7.37 - 7.46 (m, 11 H), 7.29 (d, *J* = 6.0 Hz, 1 H), 6.65 (d, *J* = 6.0 Hz, 1 H), 6.56 (brs, 1 H), 1.50 (s, 9H), 1.10 (s, 9 H); $^{13}$C nmr δ 145.38, 144.13, 140.82, 140.70, 137.27, 135.30, 130.64, 129.90, 128.61, 127.21, 127.03, 126.61, 126.35, 126.23, 119.63, 117.75, 34.04, 33.11, 29.77; EIMS m/z 392 (M$^{+}$, 78%), 377 (100), 57 (75).

**1-(Diphenyl)methylene-6-(1,1-dimethylethyl)-1*H*-indene 5b:** yellow crystalline solid, mp 177-178 °C, IR (KBr) 2964, 2873, 1601, 1488, 1450 cm$^{-1}$; $^{1}$H nmr (200 MHz) δ 7.26 - 7.48 (m, 11 H), 6.91 (dd, *J* = 8.0, 2.0 Hz, 1 H), 6.88 (d, *J* = 5.4 Hz, 1 H), 6.65 (d, *J* = 5.4 Hz, 1 H), 6.51 (d, *J* = 8.0 Hz, 1 H), 1.31 (s, 9 H); $^{13}$C nmr δ 150.60, 146.01, 144.40, 142.50, 141.52, 138.79, 131.81, 131.45, 130.55, 130.23, 129.09, 128.73, 128.52, 128.26, 127.96, 127.78, 123.06, 121.69, 117.96, 34.72, 31.44; EIMS m/z 336 (M$^{+}$, 72%), 321 (100), 279 (20).

**1-(Diphenyl)methylene-4-methoxy-1*H*-indene 5c:** Yellow semisolid, IR (CH$_2$Cl$_2$) 2940, 1556, 1478, 1435,1265, cm$^{-1}$; $^{1}$H nmr δ 7.28 - 7.46 (m, 10 H), 7.06 (d, *J* = 5.6 Hz, 1 H), 6.78 (d, *J* = 7.2 Hz, 1 H), 6.72 (d, *J* = 1.35 Hz, 1 H), 6.54 (d, *J* = 5.6 Hz, 1 H), 6.23 (d, *J* = 7.2 Hz, 1 H), 3.87 (s, 3 H); $^{13}$C nmr δ 163.28, 152.36, 142.31, 141. 53, 137.56, 131.51, 130.28, 128.49, 128.38, 128.11, 127.78, 125.69, 116.83, 109.67, 55.49; EIMS m/z, 310 (M$^{+}$, 100%), 295 (21), 279 (34), 233 (15).

**(*E*)-1-Benzylidene-4,6-bis(1,1-dimethylethyl)-1*H*-indene 5d:** Yellow crystalline solid: mp 102 - 103 °C; IR (KBr) 2768, 2684, 1455, 1414 cm$^{-1}$; $^{1}$H nmr (200 MHz) δ 7.59 - 7.69 (m, 2 H), 7.27-7.57 (m, 7 H), 6.99 (d, *J* = 5.8 Hz, 1 H), 1.49 (s, 9 H), 1.42 (s, 9 H); $^{13}$C nmr δ 147.98, 142.88, 140.13, 138.28, 137.24, 136.73, 135.24, 130.20, 128.58, 128.05, 127.60, 124.47, 121.84, 114.05, 35.59, 34.99, 31.68, 31.32; EIMS m/z 316 (M$^{+}$, 35%), 301 (100), 239 (10), 202 (33), 165 (18), 57 (32); HRMS Calcd. 316.21912, Found. 316.21888.

**(*E*),(*Z*)-1-Benzylidene-6-(1,1-dimethylethyl)-1*H*-indene 5e:** Yellow solid: IR (KBr) 2967, 2918, 1564, 1447 cm$^{-1}$; $^{1}$H nmr δ ; 6.93 - 7.67( m, 9 H) , 6.80 (d, *J* = 5.4 Hz, 1 H), 6.51 (d, *J* = 5.4 Hz, 1 H), 1.35 (s, 9 H); $^{13}$C nmr δ 137.09, 134.76, 132.64, 131.24, 130.11, 129.30, 128.58, 128.29, 128.08, 127.93, 126.20, 122.17, 118.74, 118.08, 34.81, 31.50; EIMS m/z 260 (M$^{+}$, 42%), 245 (100), 202 (32).

**(*E*)-1-[(4-Methoxyphenyl)methylene]-4,6-bis(1,1-dimethylethyl)-1*H*-indene 5f:** yellow viscous liquid, IR (film), 2965, 2873, 1606, 1515, 1255 cm$^{-1}$; $^{1}$H nmr δ 7.32 -7.75 (m, 6 H), 6.93 - 7.11 (m, 3 H), 3.88

(s, 3 H), 1.52 (s, 9 H), 1.48 (s, 9 H); $^{13}$C nmr δ 159.79, 147.74, 142.76, 138.34, 138.25, 136.43, 134.52, 131.69, 129.96, 127.51, 124.29, 121.45, 114.23, 113.82, 55.28, 35.59, 34.99, 31.68, 31.29; EIMS m/z 346 ($M^+$, 64%), 331 (100), 57 (51).

**1-[(1'-Methyl)benzylidene]-4,6-bis(1,1-dimethylethyl)-1H-indene 5g:** see ref 8.

**(E),(Z)-1-[(1'-Methyl)benzylidene-6-(1,1-dimethylethyl)-1H-indene 5h:** yellow solid, IR (KBr), 2967, 2872, 1614, 1492, 1367 cm$^{-1}$; $^1$H nmr δ 7.77 (d, $J$ = 9.0 Hz, 1H), 7.21-7.44 (m, 6H), 6.88 (s, 1H), 6.72 (d, $J$ = 5.4 Hz, 1 Hz), 6.42 (d, $J$ = 5.4, 1H), 2.72 (s, 3H), 1.38 (s, 9H); $^{13}$C nmr δ 150.21, 144.49, 144.28, 133.36, 131.00, 130.28, 129.72, 129.24, 128.67, 127.84, 127.60, 127.39, 123.57, 122.59, 121.84, 118.29, 34.72, 31.50, 22.94; EIMS m/z 274 ($M^+$, 49%), 259 (100), 215 (20).

**Dimethyl bicyclo[2.2.2]octa-2,5-diene-7,8-dioxa-1,5-bis(1,1-dimethylethyl)-2,3-dicarboxylate 7a:** Prepared according to the reported procedure.$^{10}$ Yellow crystalline solid (hexane); 88%; mp 146 °C; UV spectrum $\lambda_{max}$ (cyclohexane): 270 (ε 2269), 233 (4896), 214 (6190).

**Bicyclo[2.2.2]oct-2,5-diene-1,5-bis(1,1-dimethylethyl)-3-hydroxymethyl-7,8-dione 7b:** 3,5-di-*tert*-butyl-*o*-quinone **1a** (400 mg, 1.81 mmol) and propargyl alcohol (0.20 ml, 192 mg, 3.43 mmol) were dissolved in toluene and refluxed in an oil bath for 24 h and column chromatography using 20% EtOAc in petroleum ether afforded 461 mg (92%) of the bicyclic alcohol **7b** as a viscous yellow liquid: IR(film) 3460, 2969, 2878, 1743, cm$^{-1}$; $^1$H nmr (300 MHz) δ 6.29 (d, $J$ = 2.1 Hz, 1 H), 6.02 (d, $J$ = 2.1 Hz, 1 H), 4.34 (brs, 2 H), 4.10 (t, $J$ = 2.1 Hz, 1 H), 2.58 (brs, 1 H), 1.18 (s, 9 H), 1.12 (s, 9 H); $^{13}$C nmr δ 182.62, 182.22, 154.44, 145.17, 126.59, 122.52, 62.65, 61.77, 53.33, 35.40, 31.52, 28.08, 25.72; Anal. calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.56; H, 8.70. CIMS m/z 294 ($M^+ + NH_4^+$, 100%), 238 (10).

**Preparation of 7c and 7d:** A mixture of quinone **1a** (500 mg, 2.27 mmol) and phenyl acetylene (0.28 ml, 260 mg, 2.54 mmol) was heated neat in a sealed tube at 120 °C for 36 h. Column chromatography of the residue on silica gel using a 2% ethyl acetate in hexane afforded 570 mg (78%) of **7c** and **7d** as a mixture, and was separated by fractional crystallisation ($Et_2O$-hexane).

**2-Phenyl-1,5-bis(1,1-dimethylethyl)bicyclo[2.2.2]oct-2,5-diene-7,8-dione 7c:** Yellow crystalline solid: mp 175 -176 °C; IR (KBr) 2968, 2877, 1747, 1731, 1485, 1403,1368, 1233 cm$^{-1}$; $^1$H nmr (270 MHz) δ 7.20 ( m, 5 H) , 6.30 (d, $J$ = 6.4 Hz, 1 H), 6.20 (d, $J$ = 2.3 Hz,1 H), 4.16 (dd, $J$ = 6.4, 2.3 Hz, 1 H) ,1.17 (s, 9 H) 1.04 (s, 9 H) ;$^{13}$C nmr δ 182.96, 181.45, 153.69, 139.23, 132.63, 130.39, 127.57, 127.36, 123.79, 51.77, 35.16, 33.37, 28.45, 27.96, 27.53, 26.15; EIMS *m/z* 266 ($M^+$- 57, 14%), 251(25), 57(100).

**3-Phenyl-1,5-bis(1,1-dimethylethyl)bicyclo[2.2.2]oct-2,5-diene-7,8-dione 7d:** Orange crystals: mp 143 -144 °C; IR (KBr) 2968, 2912, 1740, 1733 cm$^{-1}$; $^1$H nmr (270 MHz) δ 7.43 ( m, 5 H), 6.60 (d, $J$ = 2.3 Hz, 1 H), 6.11 (d, $J$ =1.8 Hz,1 H), 4.62 (dd, $J$ = 2.3, 1.8 Hz, 1 H), 1.25 (s, 9 H) 1.17 (s, 9 H) ; $^{13}$C nmr δ 182.59, 181.48,154.81, 143.70, 135.55, 128.92, 127.42, 125.75, 122.53, 55.40, 35.62, 31.85, 31.48, 28.31, 26.29; EIMS m/z 266 ($M^+$ - 57, 38%), 251 (100), 57 (98); Anal. calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 82.28; H, 8.27.

**Dimethyl 3,5-bis(1,1-dimethylethyl)phthalate 8a:** Irradiation of **7a** (270 mg) as described in the typical procedure for 30 min afforded, after column chromatography on silica gel (2% EtOAc in hexane), 187 mg (82%) of **8a** as a colourless viscous liquid: IR (film) 2973, 2877, 1741, 1607,1265 cm$^{-1}$; $^1$H nmr (200 MHz) δ 7.84 (d, $J$ = 2.0Hz, 1 H), 7.72 (d, $J$ = 2.0 Hz, 1 H), 3.90 (s, 3H), 3.88 (s, 3 H),1.41 (s, 9 H), 1.34

(s, 9 H); $^{13}$C nmr δ 171.07, 166.92, 151.50, 147.14, 130.88, 128.97, 128.08, 124.62, 52.09, 52.03, 36.39, 34.75, 31.32, 30.90; EIMS m/z 306 ($M^+$, 8%), 291 (40), 275 (44), 259 (100), 57 (40).

**3,5-Bis(1,1-dimethylethyl) benzyl alcohol 8b:** The dione **7b** (448 mg) was subjected to photolytic decarbonylation (30 min) as in the case of **3a** to furnish the alcohol **8b** (314 mg, 88%) as a colourless crystalline solid, after silica gel column chromarography using 2% EtOAc in hexane as eluent: Mp 52-53 °C; IR (KBr) 3316, 2972, 2874, 1602, 1466 cm$^{-1}$; $^1$H nmr (200 MHz) δ 7.39 (d, $J$ = 1.6 Hz, 1 H), 7.23 (d, $J$ = 1.6 Hz, 2 H), 4.70 (s, 2 H), 1.67 (brs, 1 H),1.35 (s, 18 H); $^{13}$C nmr δ 150.69, 139.98, 121.27, 121.04, 65.36, 34.63, 31.32; EIMS m/z 220 ($M^+$, 17%), 205 (100), 57 (52); Anal. calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.32; H, 11.03.

**1-Phenyl-2,4-bis(1,1-dimethylethyl)benzene 8c:** Irradiation of **7c** (320 mg) as in the typical procedure for 25 min gave, after column chromatography on silica gel using hexane, 259 mg (98%) of **8c**: colourless crystalline solid: mp 60 -61 °C; IR (KBr) 2967, 2877, 1485, cm$^{-1}$; $^1$H nmr δ 7. 65 (brs, 1 H), 7.14 - 7.42 (m, 6 H), 6.01 (d, $J$ = 8.6 Hz, 1 H), 1.44 (s, 9 H), 1.28 (s, 9 H); $^{13}$C nmr δ 149.41, 146.96, 145.50, 139.12, 132.22, 130.23, 127.15, 126.35, 123.57, 121.72, 36.81, 34.72, 32.84, 31.59; EIMS m/z 266 ($M^+$, 28%), 251 (55), 195 (17), 57 (100).

**1-Phenyl-3,5-bis(1,1-dimethylethyl)benzene 8d**: Irradiation of **7d** (300 mg) as in the typical procedure for 30 min furnished, after silica gel column chromatography using hexane as eluent, 240 mg (97%) of **8d** as a colourless solid; mp 62 - 63 °C; IR (KBr) 2969, 2873, 1600, cm$^{-1}$; $^1$H nmr (200 MHz) δ 7.63 (dd, $J$ = 7.0, 1.8 Hz, 2 H), 7.42 - 7.54 (m, 5 H), 7.37 (d, $J$ = 7.0 Hz, 1 H), 1.42 (s, 18 H), $^{13}$C nmr δ 151.14, 142.64, 140.85, 128.60, 127.51, 126.97, 121.78, 121.39, 35.02, 31.62; EIMS m/z 266 ($M^+$, 34%), 251 (100), 57 (64); Anal. calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 89.55, H, 10.03

## References and notes

1. Farnia, G.; Marcuzzi, F.; Melloni, G.; Sandona, G.; Zucca, M. V. *J. Am. Chem. Soc.* **1989**, *111*, 918 and relevant references cited therein.
2. Marcuzzi, F.; Azzena, U.; Melloni, G. *J. Chem. Soc. Perkin Trans. 1* **1993**, 2957.
3. (a) Nair, V.; Kumar, S.; Williard, P. G. *Tetrahedron Lett.*, **1995**, *36*,1605. (b) Nair, V.; Kumar, S.; Rath, N. P.; Morton G. O. *Chemistry Lett.*, **1995**, 383; (c) Nair, V.; Kumar, S.; Anilkumar, G; Nair, J. S. *Tetrahedron*, **1995**, *51*, 9155.
4. a) For earlier work see: Friedrichsen, W.; Betz, M.; Buldt, E.; Jurgens, H. J.; Schmidt, R.; Schwarz, I.; Visser, K. *Liebigs. Ann. Chem.* **1978**, 440.
   b)For review see; Finley, K.T. in "The Chemistry of quinanoid compounds" Vol.2, (Ed). Patai, S,; Rappoport, Z, John Wiley, Chichester,**1988**,537.
5. For an elegant application of this methodology to the synthesis of cyclooctatetraene, see: (a) Wells,G.; Hanzawa, Y.; Paquette, L. A. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 544. For a recent report on bisdecarbonylation see: (b) Kim, S. S; Yu, Y.H; Shim, S. C; Cho, I. H. *Tetrahedon Lett.* **1994**, *35*, 9039.
6. The utility of photoextrusion in synthesis is well established. For an excellent review, see: (a) Givens, R. S. '*Organic Photochemistry*' (Ed.) Padwa, A., Marcel Dekker,**1981**, Vol. *5*, Chapter 3, p 273.

7. $CH_3CN$ as solvent improved the solubility of the adduct, but lowered the yield of photoproducts and only partial conversion was observed. Undesirable side reactions were also observed under this conditions.
8. DDQ reaction failed to give the dehydrogenated product. It is not clear why the methyl substitution in the exomethylene carbon affects the success of this reaction.
9. Interconversions of geometrical isomers (*E&Z*) of benzofulvenes is well established: (see ref. 6).
10. Liao, C. C.; Lin, H. S. *J. Chin. Chem. Soc.* **1986**, *33*, 73.
11. Nanosecond laser flash photolysis of **7c** was carried out using the 355 nm out put of a Quanta-Ray GCR-12 series Nd: YAG laser (pulse width 6 ns). Transient absorption was monitored from 300 nm to 800 nm using an Applied Physics laser kinetic spectrometer. A deoxygenated solution of **7c** (under argon) in cyclohexane having an absorbance of 0.226 at 355 nm was used for the experiment. Under these conditions, no transient species were observed.

    The authors thank Mr. C. S. Rajesh of the Photochemistry Research Unit for this experiment.

(*Received in UK* 25 *October* 1995; *revised* 30 *November* 1995; *accepted* 7 *December* 1995)